

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-155197

(43)Date of publication of application : 28.05.2002

(51)Int.Cl.

C08L 67/04

C08J 5/00

C08J 9/04

C08K 5/29

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(30)Priority

Priority number : 2000274919 Priority date : 11.09.2000 Priority country : JP

(54) BIODEGRADABLE HEAT RESISTANT RESIN COMPOSITION, AND SHEET, MOLDING, AND EXPANDED MATERIAL THEREFROM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a resin composition for an expansion material having decomposability and heat resistance.

SOLUTION: This is a resin composition comprising 50-99.9 mass % polylactic acid resin containing at least 20 mass % polylactic acid having not higher than 160,000 weight average molecular weight, and an L-form to D-form ratio of not lower than 95/5 or not higher than 5/95, and 0.1-2.5 mass % isocyanate compound. This resin composition generates in the reducing temperature process of a differential scanning calorimetry(DSC) an exothermal peak derived from crystallization of not less than 10 J/g equivalent of a polylactic acid resin at a reducing temperature rate of not less than 20°C/min.

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CLAIMS

[Claim(s)]

[Claim 1]A biodegradable heat-resistant resin composition comprising:
50 to polylactic acid system resin 99.9 mass % in which weight average molecular weight is 160,000 or less, and a mole ratio of L object and D object contains polylactic acid which is 95/5 or more and 5/95 or less in more than 20 mass %.
0.1 to isocyanate compound 2.5 mass %.

[Claim 2]The biodegradable heat-resistant resin composition according to claim 1, wherein a crystallization origin exothermic peak of 10 or more J/g occurs in polylactic resin conversion in a temperature fall process of differential scanning quantity-of-heat (DSC) measurement a temperature falling speed of 20 ** / above min.

[Claim 3]A sheet produced by carrying out melt molding of the resin composition according to claim 1 or 2.

[Claim 4]A Plastic solid acquired by carrying out melt molding of claim 1, a resin composition given in 2, or the sheet according to claim 3.

[Claim 5]Foam produced by carrying out foaming of claim 1 or a resin composition given in 2, the sheet according to claim 3, or the Plastic solid according to claim 4.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]In addition to a biodegradable function, this invention relates to the resin composition for a sheet, a Plastic solid, and foam which has heat resistance.

[0002]

[Description of the Prior Art]In recent years, the landfill places which are the last disposal centers run short, and especially the waste treatment of the plastic poses a serious problem. It is used for very many things from having the function whose plastic foam was cheap and which was excellent also in the plastic.

It is cheap, therefore almost all things are thrown away.

As these plastics, it is cheap and things, such as a mechanical strength and a product made from polystyrene whose heat resistance is comparatively high, a product made from polyethylene, and a product made from polyurethane, are used. However, since ** will

become high if these plastics are accumulated, recovery cost becomes very high, and since recycling cost is also high, a small quantity is not recycled after use, and the most is discarded.

[0003]In order to cope with a discarding treatment problem, shock absorbing material and the container made of paper are substituted, but shock absorbing material and the container made of paper are weak to *****, and the stability at the time of modification is inferior, and it is unsuitable to repeated use. For this reason, shock absorbing material or the container made of paper do not obtain a disposable fake colander, but promote exhaustion of precious forest resources.

[0004]As one of such the environmental impact restraint means, it is decomposed by the inside of the ground, and the underwater microorganism, and is included in the cyclical-change-of-materials system of a nature, development of the biodegradable polymer which does not pollute environment is desired strongly, and trial production examination of the foam, such as polybutylene succinate and a polycaprolactone, is carried out. However, the above-mentioned resolvability foam has heat resistance and an insufficient mechanical strength, and since mold occurs in the case of long-term use, practical foam cannot say it.

[0005]On the other hand, the lactic acid system polymer which has biodegradability has high safety, the combustion calorie at the time of combustion is low, and the research and development are performed briskly in recent years. Although JP,2000-7813,A and JP,2000-17039,A are indicated about the foam using these lactic acid system polymer, By increasing the content of the optical isomer to contain, these foam has improved the flowability of polylactic acid and raised fizz. However, the serious problem that foam will adhere occurred frequently at the time of the storage in the summer when it changes easily in at the time of an elevated temperature, and atmospheric temperature rises since these lactic acid system foam comprises polylactic acid of amorphism nature. In JP,9-263651,A, the method of improving the melt viscosity at the time of foaming is indicated using the polylactic acid of the ultrahigh molecular weight which added and obtained the polymers quantification agent. However, since these polylactic acid system foam does not have enough crystallinity, it does not have practical heat resistance.

[0006]

[Problem(s) to be Solved by the Invention]This invention solves the discarding treatment problem of foam, such as a product made from polystyrene, a product made from polyethylene, and a product made from polyurethane, which poses the present problem as mentioned above, The biodegradable heat-resistant resin composition which does not consume precious forest resources like the shock absorbing material made of paper or a paper made container, and can bear under the hot environments which were impossible in the conventional biodegradable foams is provided.

[0007]

[Means for Solving the Problem]As a result of repeating research wholeheartedly, this invention persons became possible [giving high crystallinity to polylactic resin by which low molecule quantification was carried out by adding an isocyanate compound], found out that an aforementioned problem was solvable, and reached this invention. Namely, the polylactic acid system resin 50 in which, as for a gist of this invention, weight average molecular weight contains polylactic acid whose mole ratios of L object and D object it is 160,000 or less and are 95/5 or more and 5/95 or less in more than 20 mass % - 99.9 mass %, It is a biodegradable heat-resistant resin composition consisting of 0.1 to

isocyanate compound 2.5 mass %.

[0008]

[Embodiment of the Invention] Hereafter, this invention is explained in detail. The biodegradable heat-resistant resin composition of this invention needs to use the polylactic acid which is biodegradable resin as the main ingredients. Although polylactic resin has the characteristic equivalent to a synthetic resin and does not change condition of use under anticipated-use environment, either, resolvability is shown under abandonment environment. And the simple nonenzymatic hydrolysis for which the initial stage of disassembly of polylactic resin does not need a microorganism serves as a subject, and a molecular weight falls. Therefore, it becomes possible to perform reduction by carrying out fixed time neglect under the environment which can hydrolyze the high biodegradable heat-resistant foam of **, and the collection after use, conveyance, and compost processing become easy.

[0009] As polylactic acid used for this invention, the copolymers or these mixtures of polylactic acid or lactic acid, and other hydroxycarboxylic acid are mentioned. As other hydroxycarboxylic acid, glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyrate, 4-hydroxyvaleric acid, 5-hydroxyvaleric acid, 6-hydroxycaproic acid, etc. are used.

[0010] Although it is the meaning of this invention that the biodegradable heat-resistant resin composition of this invention is a resin composition which uses polylactic acid as the main ingredients, and it is what can crystallize easily, differential scanning calorimeter (DSC) measurement can estimate the degree of the ease of this crystallization. Here, after a differential scanning calorimetry heats 5-8 mg of samples with a heating rate fixed from ordinary temperature to 200 ** and holds them for 3 minutes at 200 **, it measures the amount of endothermics and calorific value which are produced at the time of a series of operations cooled to ordinary temperature with a fixed temperature falling speed. And in the temperature fall process after carrying out temperature up, crystallization becomes possible at the time of the usual fabricating operation, and a heat-resistant Plastic solid is acquired, without requiring heat treatment, so that a crystallization origin exothermic peak occurs in a quick temperature falling speed. In the biodegradable heat-resistant resin composition of this invention, as for the exothermic peak of this crystallization origin, it is preferred that they are 10 or more J/g in polylactic resin conversion, and it is still more preferred that they are 15 or more J/g. The exothermic peak of this crystallization origin becomes amorphous [the great portion of polylactic acid] by polylactic resin conversion for them to be less than 10 J/g, and sufficient heat resistance is not obtained. The polylactic resin conversion said here is the value which ** (ed) calorific value of the exothermic peak by the content of the polylactic acid contained in a resin composition sample. It is preferred that the exothermic peak of this crystallization origin occurs in this invention the temperature falling speed of 20 ** / above min, it is still more preferred to generate the temperature falling speed of 30 ** / above min, and especially the thing to generate the temperature falling speed of 50 ** / above min is preferred. It is because it is very much [crystallization becomes less enough / the resin composition which the exothermic peak of crystallization origin does not generate the temperature falling speed of 20 ** / above min / as, and / heat resistance] inferior. It is required for the polylactic resin with which the biodegradable heat-resistant resin composition of this invention is presented for the mole ratio of L object and D object to contain the high crystalline polylactic acid which is 95/5 or more and 5/95 or

less, and 96/4 or more and 4/96 or less are preferred. When the mole ratio of L object and D object is less than 95/5, or when exceeding 5/95, crystallinity falls and it becomes impossible to give heat resistance.

[0011]The weight average molecular weight of the polylactic resin of the above-mentioned quantity crystallinity with which the biodegradable heat-resistant resin composition of this invention is presented needs to be 160,000 or less, and 140,000 especially or less are preferred. It is because crystallization will become remarkably slow if the weight average molecular weight of the above-mentioned quantity crystallinity polylactic acid exceeds 160,000. Although what was directly obtained by direct or ring opening polymerization may be sufficient as polylactic resin of the low molecular weight of the above-mentioned quantity crystallinity, as what remarkable crystallization generates, Especially the thing by which low molecule quantification of the weight average molecular weight was carried out by performing hydrolysis and/or pyrolysis treatment in 180,000 or more polylactic resin is preferred. The method of hydrolyzing the polylactic acid of the amount of polymers, and heating as a method of carrying out low molecule quantification, more than glass transition temperature, where moisture is included in the polylactic acid of the amount of polymers is mentioned.

[0012]It is required for the biodegradable heat-resistant resin composition of this invention to include the above-mentioned polylactic acid of high crystallinity as for more than 20 mass %, and it is preferred that more than 50 mass % contains. Crystallinity falls and it becomes impossible for the content of the polylactic acid of high crystallinity to give sufficient heat resistance by less than 20 mass %. In the biodegradable heat-resistant resin composition of this invention, as ingredients other than the above-mentioned polylactic acid of high crystallinity, Biodegradable resin, such as polylactic acid of a polycaprolactone, polyester carbonate, polyester amide, polyether ester amide, polyether ester, polybutylene succinate, and a low crystal, can be contained.

[0013]It is required for the biodegradable heat-resistant resin composition of this invention to contain an isocyanate compound as a cross linking agent. By containing an isocyanate compound, a rapid reduction of the resin melt viscosity near the melting point is eased, and change of the melt viscosity of resin accompanying change of temperature becomes small. Since the isocyanate compound has the outstanding crystallization facilitatory effect, it is indispensable to the resin composition of this invention.

[0014]As an isocyanate compound, there is an isocyanate compound of aromatic series, alicycle fellows, and an aliphatic series system, for example, as an aromatic isocyanate compound, Tolylene, diphenylmethane, naphthylene, tolidine, xylene, the isocyanate compound that makes triphenylmethane a skeleton, As the isocyanate compound which makes isophorone hydrogenation diphenylmethane a skeleton as alicycle fellows' isocyanate compound, and an isocyanate compound of aliphatic series, hexamethylene, the isocyanate compounds which make lysine a skeleton, and these mixtures are mentioned. Especially the isocyanate compound that makes xylene a skeleton also in this is preferred.

[0015]The isocyanate functional group number of an isocyanate compound is preferred in 2.0 Eq/mol or more, and preferred in especially 2.7 Eq/mol or more. This is that the functional group number of an isocyanate compound increases, and is because a thickening effect is acquired by a little addition.

[0016]The content of the isocyanate compound in a biodegradable heat-resistant resin

composition needs to be 0.1 to 2.5 mass %, and its 0.2 - 1.5 mass % is preferred. It is because biodegradability will be spoiled if the effect of the bridge construction of the content of an isocyanate compound by less than 0.1 mass % does not show up but 2.5 mass % is exceeded.

[0017]A solid state particulate matter can be contained in the biodegradable heat-resistant resin composition of this invention. As a solid state particulate matter, there are inorganic system particles and organic system particles, and as inorganic system particles Diatomaceous earth, A calcination bar light, zeolite, kaolin, bentonite, silica, clay, Glass, limestone, a calcium silicate, calcium sulfate, an aluminum oxide, It is preferred for magnesium carbonate, the second iron of carbonic acid, etc. to be mentioned, and for wood flour, starch, cellulose, a cellulosic, etc. to be raised as organic system particles, and to contain silica and talc as a solid state particulate matter in this. The above-mentioned solid state particulate matter also has the effect of distributing uniformly the air bubbles which a foaming agent generates in resin, and it becomes possible to obtain homogeneous foam.

[0018]As for the biodegradable heat-resistant resin composition of this invention, it is preferred to have the melting characteristic specific at the time of foaming. Namely, the temperature of 200 °C and the melt viscosity in 100 sec of shear rate $^{-1}$, 1.0×10^{-2} - 1.0×10^{-5} Pa-s are preferred, and 3.0×10^{-2} - 7.0×10^{-4} Pa-s, 5.0×10^{-2} - 5.0×10^{-4} Pa-s are especially more preferably preferred. Since viscosity is too high when it becomes impossible to stop air bubbles in resin and 1.0×10^{-5} Pa-s is exceeded, since viscosity is too low at less than 1.0×10^{-2} Pa-s, air bubbles cannot be formed and it cannot become practical biodegradable heat-resistant foam. A nozzle diameter is 1.0 mm and ratio of length to diameter used for measurement of melt viscosity the nozzle which is 10.

[0019]As for the hydrolysis coefficient in 50 °C of the biodegradable heat-resistant resin composition of this invention, and 95%RH, it is preferred that it is 0.005-0.15, it is still more preferred that it is 0.01-0.14, and it is preferred that it is especially 0.02-0.13. A hydrolysis coefficient is processed for six days on condition of 50 °C and 95%RH, and relative viscosity is taken along a vertical axis, it takes the number of processing dates along a horizontal axis, and the plotted slope of a line is said. If a hydrolysis coefficient is larger than 0.15, since hydrolysis will advance from immediately after foaming, it will fracture during use or before use as biodegradable heat-resistant foam. And the time which hydrolysis takes as a hydrolysis coefficient is less than 0.005 increases, and the processing time which the reduction of biodegradable heat-resistant foam takes becomes long.

[0020]It faces using the biodegradable heat-resistant resin composition of this invention, and a thermoset stabilizer, an ultraviolet ray absorbent, an antioxidant, lubricant besides being a plasticizer etc., a spray for preventing static electricity, fire retardant, light stabilizer, a filler, paints, etc. can be used together.

[0021]As a plasticizer, di-isodecyl phthalate, di-2-ethylhexyl phthalate, Dibutyl phthalate, di-isodecyl adipate, a diisononyl horse mackerel peat, A di-n-alkyl horse mackerel peat, a di-2-ethylhexyl horse mackerel peat, A diisobutyl horse mackerel peat, di-2-ethylhexyl sebacate, di-2-ethylhexyl sebacate, Dibutyl sebacate, di-2-ethyl HEISHIRU azelate, di-2-hexylazelate, Acetyl tributyl citrate, diethyl succinate, succinic acid dibutyl, Dioctyl adipate, diethyl sebacate, dibutyl sebacate, Dioctyl sebacate, azelaic acid dibutyl, trioctyl trimellitate, diethyl phthalate, polypropylene-glycol adipic acid, polyethyleneglycol

adipic acid, adipic acid butanediol, etc. are raised.

[0022] Furthermore as an antioxidant, sulfur system antioxidants, such as hindered phenolic antioxidants, such as p-t-butylhydroxytoluene and p-t-butylhydroxyanisole, distearyl thiodipropionate, and dilauryl thiodipropionate, etc. are mentioned.

[0023] As a thermoset stabilizer, as an ultraviolet ray absorbent, triphenyl phosphite, triauryl phosphite, tris nonylphenyl phosphite, etc., p-t-butylphenyl salicylate, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-2'-carboxybenzophenone, As a lubricant, the 2,4,5-trihydroxy butyrophenone etc. Aluminum stearate, As a spray for preventing static electricity, magnesium stearate, calcium stearate, zinc stearate, barium stearate, pulmic acid sodium, etc., N,n-bis(hydroxyethyl)alkylamine, diethanolamine, alkylamine, alkyl allyl sulfonate, alkyl sulfonate, etc. as fire retardant, A hexa promo cyclododecane, tris-(2,3-dichloropropyl) phosphate, pentabromophenyl allyl ether, etc. are mentioned. Titanium oxide, carbon black, etc. are mentioned as pigments.

[0024] As a foaming agent used and used for manufacturing foam using the biodegradable heat-resistant resin composition of this invention, Although not limited in particular, what is necessary is just to choose timely with the melting point and working temperature of resin to be used, and physical foaming agents, such as chemical foaming agents, such as a common organic system solubility foaming agent and an inorganic system solubility foaming agent, volatile fluid, inactive gas, hydrocarbon, chlorination carbon, halogenated hydrocarbon, can be used.

[0025] As a chemical foaming agent, p-tosyl hydrazide, a 4,4-oxyscrew (benzenesulfonyl hydrazide), Dinitrosopentamethylenetetramine, AZOJI carvone amide, hydrazo JIKARUBON amide, 5-phenyltetrazole, 4-amino urazole, lithium acetate, Sodium acetate, potassium acetate, magnesium acetate, calcium acetate, Calcium propionate, butanoic acid magnesium, sodium caprylate, Sodium caprate, lauric acid magnesium, calcium stearate, Potassium stearate, magnesium stearate, myristic acid calcium, Benzoic acid calcium, terephthalic acid potassium, calcium carbonate, sodium bicarbonate, sodium carbonate, a sodium ethoxide, potassium phenoxide, a calcium oxide, sodium oxide, magnesium oxide, etc. are mentioned.

[0026] As a physical foaming agent, methane, ethane, butane, isopentane, hexane, Cyclohexane, ethyl cyclopentane, benzene, xylene, a methyl chloride, A methylene chloride, chloroform, a carbon tetrachloride, an ethyl chloride, dichloroethane, Dichloro ethylene, Freon 14, fluorination ethyl, 4 fluorination ethane, chloro difluoroethane, Dichlorodifluoromethane, chlorotrifluoromethane, dichlorodifluoromethane, Trichlorodifluoromethane, the dichlorotetrafluoroethane, trichlorodifluoroethane, Tetrachlorodifluoroethane, a fluorobenzene, chlorobenzene, ether, methylal, an acetal, 1,4-dioxane, acetone, ethyl methyl ketone, an acetylacetone, carbon dioxide, nitrogen gas, neon, helium, a xenon, etc. are mentioned.

[0027] A foaming agent may use two or more sorts together, using only one sort. The addition rate of a foaming agent has the preferred range of 0.05 - 50 mass %. If there are few addition rates of a foaming agent than 0.05%, since foaming will hardly be produced, practical foam is not obtained. If there are more addition rates of a foaming agent than 50 mass %, since a foaming agent will not have entered into melting resin, gas will blow and come out and the foam of predetermined shape will become difficult to get, it is not desirable. Foaming auxiliaries, such as a urea system, an organic acid system, and a metal salt system, can be used together to the above foaming agent.

[0028]As for the biodegradable heat-resistant resin composition of this invention, it is preferred that heat-resistant temperature is not less than 70 **, it is more preferred that it is not less than 85 **, and it is preferred that it is especially not less than 100 **. When foam welds mutually and heat-resistant temperature uses it as a container in less than 70 ** at the time of the storage under hot environments, and transportation, it is because it changes easily with the heat of warm foodstuffs etc.

[0029]As a method of obtaining a sheet from the biodegradable heat-resistant resin composition of this invention, Generally the T-die method which carries out melt extruding from a T die is used, and any methods, such as an injection molding method and the method of heating the sheet after extrusion under application of pressure and a vacuum, and fabricating within a metallic mold, can be used as a method of acquiring a Plastic solid.

[0030]For example, a resolvability heat-resistant tray is obtained by extruding and extruding a resin composition to the tray-like metallic mold attached at the tip of an extrusion machine, simultaneously making it fabricate in an injection molding method. The die shape attached at the tip of an extrusion machine can also form the hollow which what kind of shape may be sufficient as, for example, suited the shape of the target product. Although one per tray may be sufficient as the number of these hollows, it may be formed in two or more or more packing situations in all. A sheet can be fabricated by a T die, secondary elaboration, such as a vacuum forming method, a pressure-forming method, and heat pressing, can be performed, and the resolvability heat-resistant Plastic solid of desired shape can be acquired.

[0031]As for the foam obtained using the biodegradable heat-resistant resin composition of this invention, it is preferred that it is more than twice the expansion ratio of this, and it is preferred that they are especially 5 or more times. In a twice [less than] as many thing as this, when expansion ratio uses foam as shock absorbing material, it is because sufficient buffer effect cannot be shown. Generally the cell diameter of foam affects appearance. The cell diameter of the foam obtained by this invention is 3 mm or less, and is 1 mm or less more preferably, and especially its 0.5 mm or less is preferred. Appearance becomes less good when there is a cell with the cell diameter of greater than 3 mm.

[0032]Any methods, such as the method of making it heat and foam under the extrusion-foaming method made to foam simultaneously with extrusion molding as a method of manufacturing foam using the biodegradable heat-resistant resin composition of this invention, the foaming method by an injection molding, the application of pressure after extrusion molding, and ordinary pressure, can be used.

[0033]For example, in an extrusion-foaming method, a biodegradable heat-resistant foaming tray is obtained by extruding and extruding resin to the tray-like metallic mold attached at the tip of an extrusion machine, simultaneously carrying out foaming. The die shape attached at the tip of an extrusion machine can also form the hollow which what kind of shape may be sufficient as, for example, suited the shape of the target product. Although one per tray may be sufficient as the number of these hollows, it may be formed in two or more or more packing situations in all. Sheet shaped foam can be fabricated by a foaming method, secondary elaboration, such as a vacuum forming method, a pressure-forming method, and heat pressing, can be performed, and the biodegradable heat-resistant foam of desired shape can be obtained.

[0034]There is a method in which the outer-ring-of-spiral-wound-gasket die which provided many nozzles on the circumference, and an inner ring die carry out extrusion foaming from the circular rotating die which rotates to an opposite direction mutually as an example which manufactures the biodegradable heat-resistant foam of net shape. By forming many foamed fine strips, making this intersect mutually the foaming strand of a large number extruded from the outer-ring-of-spiral-wound-gasket die, and making it weld immediately after that extrusion by this method, The telescopic foaming network of stitch structure can be formed, it can clear in the shape of a request of this after cooling, and the biodegradable heat-resistant foam of net shape can be obtained.

[0035]When obtaining a foamed particle, it impregnates with a foaming agent and a foaming auxiliary, after making the biodegradable heat-resistant resin composition of this invention into a pellet type or bead-like particles. Usually make the impregnated particles into a foamed particle 10 to 50 times the expansion ratio of this by the first foaming with heating, and subsequently to a metallic mold they are filled up with these, heat them again, are made to foam the 2nd order, and let them be desired foam. Although the usual heating method can be used for the heating method in primary foaming and secondary foaming, it is preferred to use a steam with large calorific capacity.

[0036]The Plastic solid and foam which are obtained from the biodegradable heat-resistant resin composition of this invention, For example, a lunch box, tableware, the cup filled with boiling water like cup ramen noodles, the cup of coffee or tea, food-grade containers, such as a fresh fish, vegetables and fruits, tofu, and a daily dish, a tray, and fatty tuna -- it is used as buffer containers and shock absorbing material, such as a box, a container for dairy products, home electronics, precision products, an industrial commodity, protection-from-light material, a sound insulating material, thermal insulation, a filter, and a cushioning material.

[0037]

[Example]Next, an example explains this invention concretely. The test method used in the example and the comparative example is as follows. The low-molecular-weight polylactic acid of high crystallinity used for this invention was obtained by fusing the polylactic acid of the weight average molecular weight 200,000, making water contact, and hydrolyzing.

(1) In the amount of samples of 7 mg, the exothermic peak of the crystallization origin at the time of a temperature fall was observed using the differential scanning calorimetric measurement PerkinElmer, Inc. make 7 series DSC measurement device, and the maximum temperature falling speed which the exothermic peak of 10 or more J/g generates in polylactic acid conversion was investigated.

(2) It carried out by the method of starting a heat-resistant test profitable **** constituent and foam in 10-mm³-mm length of 125 mm in thickness, and applying to JIS K7195, and the HITOZAGU value made the maximum temperature used as less than 10 mm heat-resistant temperature. [in width]

(3) The hydrolysis test profitable **** constituent was processed for six days on condition of 50 ** and 95%RH, and relative viscosity was taken along the vertical axis, the number of processing dates was taken along the horizontal axis, and it asked for the plotted slope of a line. When this inclination was larger than 0 and 0.15, it carried out the case where it was 0.005-0.15 to it being x and less than 0.005 with x.

(4) Five sections of the evaluation profitable **** foam of a foaming cell are measured

by light microscope observation, All the foamed cell diameters made the thing below 0.5 mm O, the maximum of the foamed cell diameter made O the thing below 0.5 mm or more 3 mm, the maximum of the foamed cell diameter made ** the thing below not less than 3 mm 6 mm, and the foam in which a not less than 6-mm thing exists was made into x.

(5) The measurement weight average molecular weight of weight average molecular weight was measured with gel permeation chromatography (GPC), and was shown as a polystyrene reduced property.

[0038]With the compounding ratio shown in the example 1 table 1, melting mixing was carried out with the single screw extruder of cylinder 40 mm, and ratio-of-length-to-diameter=36, it extruded from the T die, and the constituent sheet with a 1-mm width [in thickness] of 380 mm was obtained. [in diameter] Temperature conditions were 200 ** of supplying zone, and plasticization zone 120**, 190 ** of melting zones, and 105-215 ** of die parts. The heat test result of the obtained sheet is shown in Table 1. After carrying out melting mixing with the single screw extruder of cylinder 40 mm, and ratio-of-length-to-diameter=36 and doing 5 mass % press fit of butane as a foaming agent from the barrel middle with the compounding ratio shown in Table 1, it extruded from the T die and the foaming sheet with a 3-mm width [in thickness] of 380 mm was obtained. [in diameter] Temperature conditions were 200 ** of supplying zone, and plasticization zone 120**, 190 ** of melting zones, and 105-215 ** of die parts. The test result of the obtained foaming sheet is shown in Table 1.

[0039]The sheet and the foaming sheet were obtained by the same method as Example 1 with the compounding ratio shown in the one to Examples 2-16 and comparative example 10 tables 1 and 2. The test result of the obtained sheet and a foaming sheet is shown in Tables 1 and 2.

[0040]With the compounding ratio shown in the 17 to example 19 table 1, the mixture which carried out AZOI carvone amide as a foaming agent, and did 3 mass % addition of urea as 10 mass % and a foaming auxiliary was mixed from the barrel middle, it extruded from the T die, and the unfoamed sheet with a 0.2-mm width [in thickness] of 380 mm was obtained. Temperature conditions were 200 ** of supplying zone, and plasticization zone 120**, 190 ** of melting zones, and 105-215 ** of die parts. And one side cut down the obtained unfoamed sheet for the square which is 200 mm, and foam was obtained by neglecting it for 10 to 60 minutes, and carrying out heat foaming into 170 ** oven. The test result of the obtained foam is shown in Table 1.

[0041]Using the 2 axis kneading machine (PCM30, Ikegai Corp. make), it kneaded by 180 ** of cylinder temperatures, and each resin composition was obtained so that it might become a compounding ratio shown in the 20 to example 22 table 1. After teaching isopentane 1200 mass part and methanol 240 mass part to the revolving reaction vessel and sealing these resin compositions as resin composition 2000 mass part and a foaming agent to it, temperature up was carried out at a rate with a heating rate of 20 **/hour by ten number-of-rotations/of a reaction vessel, and it held at 70 ** for 1 hour. Then, it cools to a room temperature, a foaming agent impregnating resin constituent is taken out, pre-expansion was carried out with the steam (92 **, 1 minute) after desiccation, pre-expansion particles were obtained with the foam molding machine after aging on the 1st, and the foaming object was acquired on water-vapor-pressure 0.5 kg/cm² and the conditions for cooking time 30 seconds. The test result of the obtained foam is shown in

Table 1.

[0042]

[Table 1]

	樹脂組成物											発泡シート			
	ポリ乳酸			固体状粒子物質		他成分		架橋剤		最大降 温速度 ℃/min	耐熱 温度 ℃	加水 分解	耐熱 温度 ℃	セル 状態	
	モル比 L体/D体	重量平均 分子量	含有量 質量%	名称	含有量 質量%	名称	含有量 質量%	名称	官能基数 当量/g						含有量 質量%
実施例 1	99.5/0.5	13 万	99.1	—	—	—	—	TDI	2	0.9	100	130	○	140	○
実施例 2	99/1	13 万	99.1	—	—	—	—	TDI	2	0.9	80	130	○	130	○
実施例 3	96/4	13 万	99.1	—	—	—	—	TDI	2	0.9	70	110	○	120	○
実施例 4	1/99	13 万	99.1	—	—	—	—	TDI	2	0.9	80	130	○	130	○
実施例 5	99/1	14 万	99.1	—	—	—	—	TDI	2	0.9	80	110	○	110	○
実施例 6	99/1	12 万	99.1	—	—	—	—	TDI	2	0.9	80	120	○	130	○
実施例 7	99/1	9 万	99.1	—	—	—	—	TDI	2	0.9	80	130	○	130	○
実施例 8	99/1	8 万	99.1	—	—	—	—	TDI	2	0.9	80	120	○	130	○
実施例 9	99/1	13 万	99.1	—	—	—	—	TDI	3.2	0.9	80	110	○	120	○
実施例 10	99/1	13 万	99.1	—	—	—	—	BDI	3.2	0.9	80	110	○	120	○
実施例 11	99/1	13 万	99.1	—	—	—	—	TDI	3	0.9	80	110	○	120	○
実施例 12	99/1	10 万	90	—	—	PLA1	49.1	TDI	3.2	0.9	50	100	○	110	○
実施例 13	99/1	10 万	70	—	—	PLA1	29.1	TDI	3.2	0.9	50	100	○	110	○
実施例 14	99/1	10 万	90	—	—	ATBC	9.1	TDI	3.2	0.9	50	100	○	110	○
実施例 15	99/1	10 万	97.1	タルク	2	—	—	BDI	3	0.9	50	100	○	100	○
実施例 16	99/1	10 万	94.1	タルク	5	—	—	BDI	3	0.9	50	100	○	100	○
実施例 17	99/1	10 万	56	—	—	PLA1	44.1	TDI	3.2	0.9	50	100	○	110	○
実施例 18	99/1	10 万	70	—	—	PLA1	29.1	TDI	3.2	0.9	50	100	○	110	○
実施例 19	99/1	10 万	90	—	—	ATBC	9.1	TDI	3.2	0.9	50	100	○	110	○
実施例 20	99/1	10 万	80	—	—	PLA1	49.1	TDI	3.2	0.9	50	100	○	110	○
実施例 21	99/1	10 万	70	—	—	PLA1	29.1	TDI	3.2	0.9	50	100	○	110	○
実施例 22	99/1	10 万	90	—	—	ATBC	9.1	TDI	3.2	0.9	50	100	○	110	○

[0043]

[Table 2]

	樹脂組成物														発泡シート	
	モル比 L/D体	ポリ乳酸 成分平均 分子量	含有量 質量%	固体状粒子物質		他成分		架橋剤		最大降 温速度 ℃/min	耐熱 温度 ℃	加水 分解	耐熱 温度 ℃	セル 状態		
				名称	含有量 質量%	名称	含有量 質量%	名称	官能基数 当量/g						含有量 質量%	
比較例 1	90/10	10 万	99.1	—	—	—	—	TDI	3	0.9	2	60	○	70	△	
比較例 2	80/20	10 万	99.1	—	—	—	—	TDI	3	0.9	2	60	○	70	△	
比較例 3	99/1	18 万	99.1	—	—	—	—	TDI	3	0.9	5	60	○	70	△	
比較例 4	99/1	22 万	99.1	—	—	—	—	TDI	2	0.9	2	60	○	70	△	
比較例 5	99/1	10 万	99.1	—	—	—	—	2td	2	0.9	2	60	○	70	×	
比較例 6	99/1	10 万	100	—	—	—	—	—	—	—	2	60	○	70	×	
比較例 7	99/1	10 万	95	タルク	5	—	—	—	—	—	2	60	○	70	×	
比較例 8	99/1	10 万	90	タルク	10	—	—	—	—	—	2	60	○	70	×	
比較例 9	99/1	10 万	85	タルク	15	—	—	—	—	—	2	60	○	70	×	
比較例 10	99/1	15 万	97	—	—	—	—	TDI	2	0.9	3	80	120	×	130	○

BDI:ヘキサメチレンジイソシアネート系化合物、TDI:キシレンジイソシアネート系化合物、TDI:トリレンジイソシアネート系化合物

TDI:2,4-ジメチル-2,5-ビス(4-ヒドロキシベンジル)-5-ノルボルネン-3-オール

PLA1:ポリ乳酸 (モル比 L 体/D 体):95/5、重量平均分子量:10 万)

ATBC:アセチルトリブチルシレート

[0044]Each heat-resistant temperature of the sheet and foam which were obtained in Examples 1-16 is not less than 100 **.

It had sufficient heat resistance and hydrolysis nature, and the foaming cell was also uniformly detailed.

On the other hand, in the comparative examples 1-9, heat-resistant temperature was 70 ** or less, and the foaming cell grew large, and it was lacking in practicality. Hydrolysis became slow, although it had heat resistance sufficient in the comparative example 10 and the foaming cell was also uniformly detailed. Each heat-resistant temperature of the

foam obtained by the method of Examples 17-22 is not less than 100 **, and has sufficient heat resistance.

The foaming cell was also uniformly detailed.

[0045]

[Effect of the Invention]The polylactic acid system resin 50 in which, as for the biodegradable heat-resistant resin composition of this invention, the mole ratio of L object and D object contains [weight average molecular weight] 95/5 or more and 5/95 or less polylactic acid or less by 160,000 in more than 20 mass % - 99.9 mass %, Foam with the performance in use of high heat resistance can be offered because an isocyanate compound considers it as 0.1 - 2.5 mass %. In order that the biodegradable heat-resistant resin composition of this invention may use polylactic resin as the main raw material, decomposition by compost is not only possible, but it is performing hydrolysis treatment after use, It can be called the very environment-friendly biodegradable heat-resistant resin composition which solves the waste disposal problems of foam, such as a product made from polystyrene which reduction becomes possible, and conveyance and accumulation become easy, and poses the present problem, a product made from polyethylene, and polyurethane.

[Translation done.]